

wherein at least one of R_1 , R_2 , R_3 and R_4 in the chemical formula (I) is/are an aliphatic hydrocarbon group (such as an alkyl group, alkenyl group or alkynyl group), aryl group, alkoxy group, aryloxy group, acyl group, ester group, alkyloxycarbonyl group, aryloxycarbonyl group, carboxyl group, formyl group, hydroxyl group, halogen group, amino group, imino group, amide group, cyano group, silyl group, mercapto group, sulfide group, disulfide group or sulfonyl group, or a functional group containing 2 or more groups thereof, and the other(s) is/are a hydrogen atom, some of Xs, that are two or more, are a halogen group and the other(s) is/are a hydrogen atom, and k is an integer of 1 to 5.

R_3 and R_4 are preferably each hydrogen atom.

It is preferable that at least one of the combinations (R_1 and R_2) and (R_3 and R_4) forms a cyclic structure, after R_1 and R_2 or R_3 and R_4 are bound to each other.

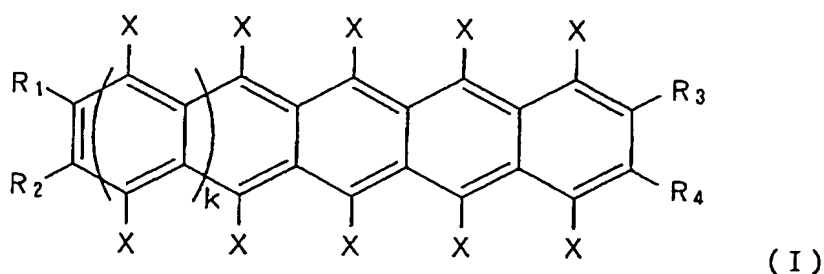
Moreover, R_1 , R_2 , R_3 and R_4 preferably have 1 to 15, more preferably 2 to 15, and particularly preferably 2 to 6 carbon atoms, when they are functional groups.

It is also preferable that an even number of Xs are each a halogen group, at least 2 of which are bound to the same

acene ring. It is particularly preferable that two of Xs are each a halogen group bound to the same acene ring.

Still more, k is preferably 1 or 2.

The organic semiconductor thin film of the present
5 invention is made of a polyacene compound having a structure represented by the following chemical formula (I) and has crystallinity.



10

In the chemical formula (I), at least one of R₁, R₂, R₃ and R₄ is/are an aliphatic hydrocarbon group (such as an alkyl group, alkenyl group or alkynyl group), aryl group, alkoxy group, aryloxy group, acyl group, ester group,
15 alkyloxycarbonyl group, aryloxycarbonyl group, carboxyl group, formyl group, hydroxyl group, halogen group, amino group, imino group, amide group, cyano group, silyl group, mercapto group, sulfide group, disulfide group or sulfonyl group, or a functional group containing 2 or more groups thereof, and
20 the other(s) is/are a hydrogen atom. In the chemical formula, some of Xs is/are a halogen group and the other(s) is/are a hydrogen atom. Moreover, k is an integer of 1 to 5.

It is preferable that R₃ and R₄ in the chemical formula (I) are each a hydrogen atom. It is also preferable that at

least one of the combinations (R_1 and R_2) and (R_3 and R_4) forms a cyclic structure, after R_1 and R_2 or R_3 and R_4 are bound to each other. Moreover, R_1 , R_2 , R_3 and R_4 preferably have 1 to 15, more preferably 2 to 15, particularly preferably 2 to 6 carbon atoms, when they are functional groups. It is also preferable that an even number of Xs are each a halogen group, at least two of which are bound to the same acene ring. It is particularly preferable that two of Xs are each a halogen group bound to the same acene ring. Still more, k is preferably 1 or 2.

It is a crystalline, organic semiconductor thin film formed on a substrate, the major axis of the molecule of the compound preferably being oriented toward a right angle to the substrate surface.

Moreover, at least part of the organic semiconductor device of the present invention is composed of the organic semiconductor thin film of the present invention.

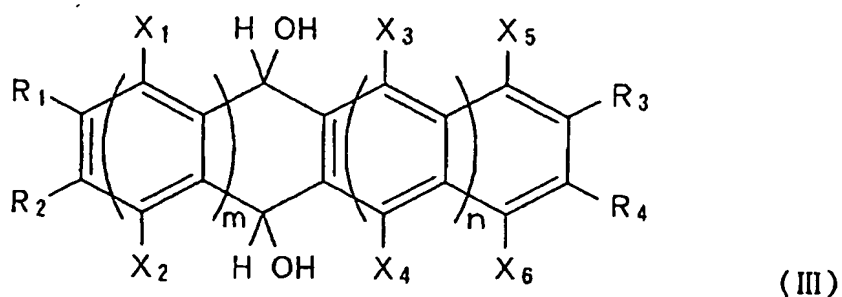
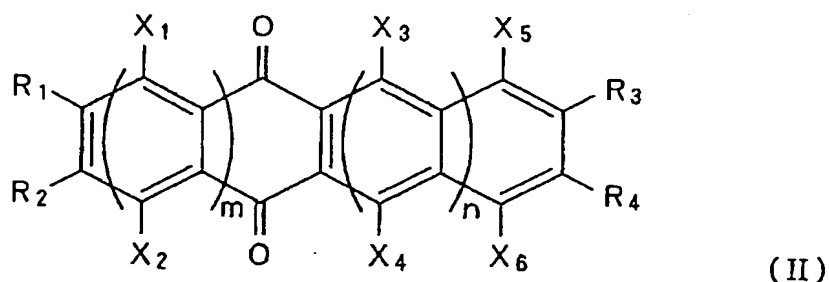
Still more, the transistor of the present invention has a gate electrode, dielectric layer, source electrode, drain electrode and semiconductor layer, wherein the semiconductor layer is composed of the organic semiconductor thin film of the present invention.

The method for producing the polyacene compound of the present invention comprises reducing a polyacenequinone derivative into a hydroxypolyacene derivative, and then halogenating and aromatizing the hydroxypolyacene derivative into a polyacene compound having a structure represented by the above-described chemical formula (I). The

polyacenequinone derivative has a chemical structure corresponding to that of a polyacene compound of the above-described chemical formula (I), has the same number of 6-membered rings and the same R_1 , R_2 , R_3 and R_4 , and has the
5 carbonyl carbon of quinine, the carbon atom of which will be bound to a halogen group, when it is converted into the polyacene compound. The

hydroxypolyacene derivative has a chemical structure corresponding to that of a polyacene compound of the above-described chemical formula (I), has the same number of 6-membered rings and the same R_1 , R_2 , R_3 and R_4 , and has a carbon atom bound to a hydroxyl group and hydrogen atom, which will be bound to a halogen group, when it is converted into the polyacene compound.

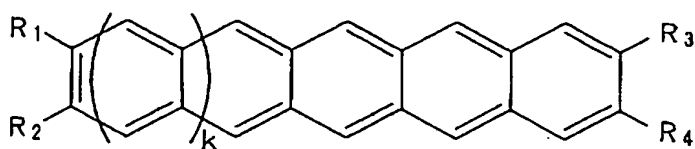
The method for producing the polyacene compound of the present invention comprises reducing a polyacenequinone derivative having a structure represented by the chemical formula (II) into a hydroxypolyacene derivative having a structure represented by the chemical formula (III), and then halogenating and aromatizing the hydroxypolyacene derivative to produce a polyacene compound having a structure represented by the above-described chemical formula (I),



wherein at least one of R_1 , R_2 , R_3 and R_4 in the chemical formulas (II) and (III) is/are an aliphatic hydrocarbon group (such as an alkyl group, alkenyl group or alkynyl group), aryl group, alkoxy group, aryloxy group, acyl group, ester group, alkyloxycarbonyl group, aryloxycarbonyl group, carboxyl group, formyl group, hydroxyl group, halogen group, amino group, imino group, amide group, cyano group, silyl group, mercapto group, sulfide group, disulfide group or sulfonyl group, or a functional group containing 2 or more groups thereof, and the other(s) is/are a hydrogen atom, X_1 , X_2 , X_3 , X_4 , X_5 and X_6 in the chemical formulas (II) and (III) are each a halogen group or hydrogen atom, unless all of X_1 , X_2 , X_3 , X_4 , X_5 and X_6 are each a halogen group, m is an integer of 2 or more, and $m+n$ is an integer of 3 to 7.

In the chemical formula (I), it is preferable that R_3 and R_4 are each a hydrogen atom. It is also preferable that at least one of the combinations (R_1 and R_2) and (R_3 and R_4) forms a cyclic structure, after R_1 and R_2 or R_3 and R_4 are bound to each other. Moreover, R_1 , R_2 , R_3 and R_4 preferably have 1 to 15, more preferably 2 to 15, particularly preferably 2 to 6 carbon atoms, when they are functional groups. It is also preferable that an even number of X s are each a halogen group, at least two of which are bound to the same acene ring. It is particularly preferable that two of X s are each a halogen group bound to the same acene ring. Still more, k is preferably 1 or 2.

The hydroxypolyacene derivative of the present invention has a chemical structure corresponding to that of the polyacene, represented by the chemical formula (IV). It has the same number of 6-membered rings and the same R_1 , R_2 , R_3 and R_4 , and
5 has at least one carbon atom, except for the one to which R_1 , R_2 , R_3 or R_4 will bound when it is converted into the polyacene, bound to a hydroxyl group and hydrogen atom.



(IV)

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In the chemical formula (IV), at least one of R_1 , R_2 , R_3 and R_4 is/are an aliphatic hydrocarbon group (such as an alkyl group, alkenyl group or alkynyl group), aryl group, alkoxy group, aryloxy group, acyl group, ester group, alkyloxycarbonyl group, aryloxycarbonyl group, carboxyl group, formyl group, hydroxyl group, halogen group, amino group, imino group, amide group, cyano group, silyl group, mercapto group, sulfide group, disulfide group or sulfonyl group, or a functional group containing 2 or more groups thereof, and the other(s) is/are a hydrogen atom. Moreover, k is an integer of 1 to 5.

The hydroxypolyacene derivative of the present invention has a chemical structure represented by the chemical formula (III).

Moreover, in the display device of the present invention, which is provided with pixel planes each composed of a number of pixels, each of the pixels is provided with the organic semiconductor device or transistor of the present invention as described above.

An electrode, dielectric layer and semiconductor layer are preferably formed in the organic semiconductor device or transistor by printing or coating of a liquid.

The polyacene compound of the present invention has a long and thin polyacene skeleton with functional groups at one or both ends of the major axis and with halogen groups on the sides. The inventors of the present invention have considered that a polyacene compound can have an increased solubility in solvents when substituted with functional groups

at one or both end of the major axis and improved oxidation resistance when substituted with halogen groups on the sides, reaching the novel polyacene compound of the present invention, represented by the chemical formula (I).

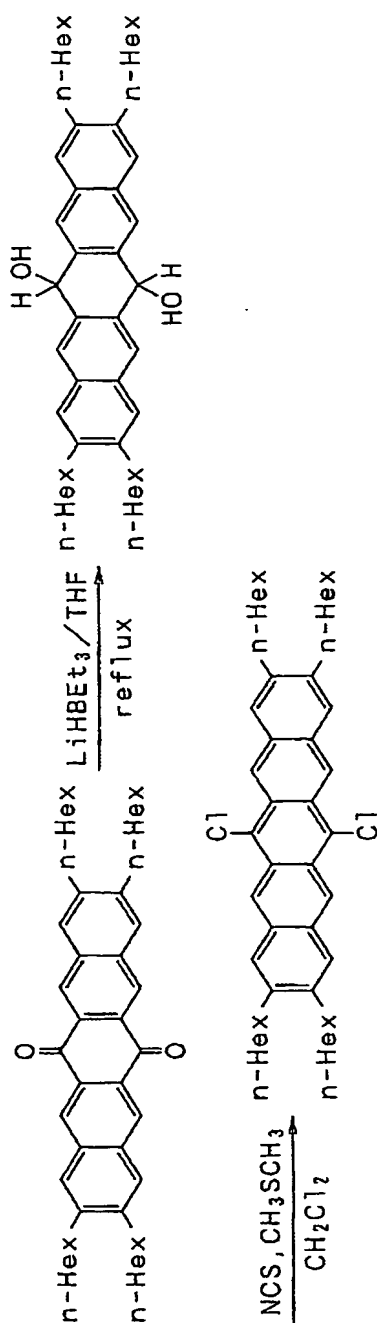
- 5 They have found that the polyacene compound and thin film thereof of the present invention exhibit a mobility equivalent to or higher than that of pentacene, known to exhibit the highest mobility among the conventional organic materials. They also

The organic semiconductor device of the present invention can be also used for a variety of sensors, e.g., gas sensor, biosensor, blood sensor, immunization sensor, artificial retina, taste sensor and so forth. Generally, the organic semiconductor thin film for the organic semiconductor device analyzes an object to be measured by change in resistance values of the thin film evolving when it is brought into contact with or close to the object.

The present invention is described in more detail by
10 EXAMPLES.

<EXAMPLE 1: Synthesis of
6,13-dichloro-2,3,9,10-tetrahexylpentacene>
<Synthesis of intermediate>

A solution of 649 mg of
15 2,3,9,10-tetrahexyl-6,13-pentacenequinone dissolved in 30 mL
of tetrahydrofuran (THF) was added to 5 mL of a 1 mol/1000
mL THF solution of lithium triethylborohydride, and the mixture
was heated for 12 hours under reflux in a nitrogen atmosphere.
The resulting solution was neutralized with diluted aqueous
20 hydrochloric acid, and the organic phase was separated,
concentrated and dried under a vacuum to produce
2,3,9,10-tetrahexyl-6,13-dihydro-6,13-dihydroxypentacene
almost stoichiometrically (see the following reaction
formula).



The resulting
 2,3,9,10-tetrahexyl-6,13-dihydro-6,13-dihydroxypentacene
 5 was analyzed by mass spectrometry. The results are given below.

FAB-MS (NBA) : m/z=649

Moreover, it was analyzed by nuclear magnetic resonance spectroscopy (NMR) at room temperature with deuterated chloroform as a solvent. The results are given below.

¹H-NMR (ppm): δ0.88-0.91 (m, 12H), 1.32-1.35 (m, 16H),
5 1.48-1.52 (m, 8H), 1.63-1.67 (m, 8H), 2.75 (t, 8H), 5.74 (s,
2H), 7.58 (s, 4H), 7.80 (s, 4H)

<Method for producing polyacene compound>

N-chlorosuccinimide (382 mg) was dissolved in 40 mL of dichloromethane in a nitrogen atmosphere, and the resulting
10 solution was cooled to -20°C, added to 0.32 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the resulting solution was added to a solution of 231 mg of 2,3,9,10-tetrahexyl-6,13-dihydro-6,13-dihydroxypentacene dissolved in 20 mL of dichloromethane dropwise, and then the
15 reaction was carried out for 18 hours while being warmed up to room temperature (see the above reaction formula).

The reaction system was added to water to terminate the reaction. The reaction product was extracted with chloroform, and the organic phase separated was washed with a saturated
20 NaCl aqueous solution and dried with magnesium sulfate. The organic phase was distilled under a vacuum to remove the organic solvent, and the resulting residue was reprecipitated in a mixed solvent of benzene and n-hexane. This produced 74 mg of pure 6,13-dichloro-2,3,9,10-tetrahexylpentacene in a
25 yield of 30%.

The resulting 6,13-dichloro-2,3,9,10-tetrahexylpentacene was analyzed by mass spectrometry. The results are given below.

for 24 hours under reflux in a nitrogen atmosphere. The resulting solution was neutralized with diluted aqueous hydrochloric acid, and the organic phase was separated, concentrated and dried under a vacuum to produce

5 6,13-dihydro-6,13-dihydroxy-2,3,9,10-tetrapropylpentacene almost stoichiometrically.

The resulting 6,13-dihydro-6,13-dihydroxy-2,3,9,10-tetrapropylpentacene was analyzed by nuclear magnetic resonance spectroscopy (NMR) at room temperature with deuterated chloroform as a solvent. The results are given below.

$^1\text{H-NMR}$ (ppm): δ 1.05 (t, 12H), 1.67-1.77 (m, 8H), 2.76 (t, 8H), 5.78 (s, 2H), 7.61 (s, 4H), 7.81 (s, 4H)

<Method for producing polyacene compound>

15 N-chlorosuccinimide (800 mg) was dissolved in 45 mL of dichloromethane in a nitrogen atmosphere, and the resulting solution was cooled to -20°C , added to 0.66 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the resulting solution was added to a solution of 361 mg of 20 6,13-dihydro-6,13-dihydroxy-2,3,9,10-tetrapropylpentacene dissolved in 35 mL of dichloromethane dropwise, and then the reaction was carried out for 18 hours while being warmed up to room temperature.

The reaction system was added to water to terminate the 25 reaction. The reaction product was extracted with chloroform, and the organic phase separated was washed with a saturated NaCl aqueous solution and dried with magnesium sulfate. The organic phase was distilled under a vacuum to remove the organic

A solution of 314 mg of 2,3-dipropyl-6,13-pentacenequinone dissolved in 60 mL of THF was added to 6 mL of a 1 mol/1000 mL THF solution of lithium triethylborohydride, and the mixture was heated for 20 hours under reflux in a nitrogen atmosphere. The resulting solution was neutralized with diluted aqueous hydrochloric acid, and the organic phase was separated, concentrated and dried under a vacuum to produce 6,13-dihydro-6,13-dihydroxy-2,3-dipropylpentacene almost stoichiometrically.

<Method for producing polyacene compound>

N-chlorosuccinimide (1.0 g) was dissolved in 60 mL of dichloromethane in a nitrogen atmosphere, and the resulting solution was cooled to -20°C, added to 0.83 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the resulting solution was added to a solution of 317 mg of 6,13-dihydro-6,13-dihydroxy-2,3-dipropylpentacene dissolved in 50 mL of dichloromethane dropwise, and then the reaction was carried out for 18 hours while being warmed up to room temperature.

The reaction system was added to water to terminate the reaction. The reaction product was extracted with chloroform, and the organic phase separated was washed with a saturated NaCl aqueous solution and dried with magnesium sulfate. The organic phase was distilled under a vacuum to remove the organic solvent, and the resulting residue was reprecipitated in ethanol. This produced 17 mg of pure 6,13-dichloro-2,3-dipropylpentacene in a yield of 5%.

The resulting 6,13-dichloro-2,3-dipropylpentacene was analyzed by mass spectrometry. The results are given below.

a vacuum to produce
2,3-dihexyl-6,13-dihydro-6,13-dihydroxypentacene almost
stoichiometrically.

<Method for producing polyacene compound>

5 N-chlorosuccinimide (780 mg) was dissolved in 40 mL of
dichloromethane in a nitrogen atmosphere, and the resulting
solution was cooled to -20°C, added to 0.64 mL of dimethyl
sulfide dropwise, and stirred for 10 minutes. Then, the
resulting solution was added to a solution of 336 mg of
10 2,3-dihexyl-6,13-dihydro-6,13-dihydroxypentacene
dissolved in 40 mL of dichloromethane dropwise, and then the
reaction was carried out for 18 hours while being warmed up
to room temperature.

The reaction system was added to water to terminate the
15 reaction. The reaction product was extracted with chloroform,
and the organic phase separated was washed with a saturated
NaCl aqueous solution and dried with magnesium sulfate. The
organic phase was distilled under a vacuum to remove the organic
solvent, and the resulting residue was reprecipitated in
20 ethanol. This produced 35 mg of pure
6,13-dichloro-2,3-dihexylpentacene in a yield of 10%.

The resulting 6,13-dichloro-2,3-dihexylpentacene was
analyzed by mass spectrometry. The results are given below.

FAB-HRMS (NBA): $m/z=514.2193$ (calculated value:
25 514.2194)

Moreover, it was analyzed by nuclear magnetic resonance
spectroscopy (NMR) at room temperature with deuterated
chloroform as a solvent. The results are given below.

50 μm (channel length). The pattern is 500 μm long (channel width).

The silicon substrate with the patterned electrodes was coated with a thin film of 6,13-dichloro-2,3-dihexylpentacene by spin coating, similar to the above, to form a transistor structure.

The transistor was analyzed for current/voltage curves between the source and drain electrodes with the substrate as the gate, where the gate voltage was changed at 10 V intervals from -10 to -40 V. It was observed that the drain current was saturated as the drain voltage increased. Mobility determined from gate voltage dependence in the current saturated region was $9 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$.

<EXAMPLE 5: Synthesis of
6,13-dibromo-2,3,9,10-tetrahexylpentacene>
<Synthesis of intermediate>

2,3,9,10-tetrahexyl-6,13-dihydro-6,13-dihydroxypentacene was prepared in the same manner as in EXAMPLE 1.

<Method for producing polyacene compound>

N-bromosuccinimide (338 mg) was dissolved in 20 mL of THF in a nitrogen atmosphere, and the resulting solution was cooled to -20°C , added to 0.20 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the solution was added to a solution of 150 mg of
2,3,9,10-tetrahexyl-6,13-dihydro-6,13-dihydroxypentacene dissolved in 10 mL of THF dropwise, and then the reaction was carried out for 18 hours while being warmed up to room temperature.

Mobility determined from gate voltage dependence in the current saturated region was $0.014 \text{ cm}^2/\text{V}\cdot\text{s}$.

<EXAMPLE 6: Synthesis of

6,13-dibromo-2,3,9,10-tetrapropylpentacene>

5 <Synthesis of intermediate>

6,13-dihydro-6,13-dihydroxy-2,3,9,10-tetrapropylpentacene was prepared in the same manner as in EXAMPLE 2.

<Method for producing polyacene compound>

N-bromosuccinimide (462 mg) was dissolved in 20 mL of
10 THF in a nitrogen atmosphere, and the resulting solution was cooled to -20°C , added to 0.28 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the solution was added to a solution of 150 mg of
6,13-dihydro-6,13-dihydroxy-2,3,9,10-tetrapropylpentacene
15 dissolved in 15 mL of THF dropwise, and then the reaction was carried out for 18 hours while being warmed up to room temperature.

The reaction product was distilled under a vacuum to remove the organic solvent, and the resulting residue was added to
20 *n*-hexane and filtered. The residue was washed with acetonitrile and then with a 1/1 mixed solvent of *n*-hexane and benzene. This produced 37 mg of pure
6,13-dibromo-2,3,9,10-tetrapropylpentacene in a yield of 20%.

25 The resulting 6,13-dibromo-2,3,9,10-tetrapropylpentacene was analyzed by mass spectrometry. The results are given below.

FAB-HRMS (NBA): $m/z=606, 604, 602$

electrodes. The gold electrode pattern comprises strips running in parallel to each other, spaced from each other by 50 μm (channel length). The pattern is 500 μm long (channel width).

5 The silicon substrate with the patterned electrodes was coated with a thin film of 6,13-dibromo-2,3,9,10-tetrapropylpentacene, in a manner similar to the above, to form a transistor structure.

10 The transistor was analyzed for current/voltage curve between the source and drain electrodes with the silicon substrate as the gate, where the gate voltage was changed at 10 V intervals from -10 to -40 V. It was observed that the drain current was saturated as the drain voltage increased. Mobility determined from gate voltage dependence in the current saturated region was 0.05 $\text{cm}^2/\text{V}\cdot\text{s}$.

<EXAMPLE 7: Synthesis of 6,13-dibromo-2,3-dipropylpentacene>
<Synthesis of intermediate>

6,13-dihydro-6,13-dihydroxy-2,3-dipropylpentacene was prepared in the same manner as in EXAMPLE 3.

20 <Method for producing polyacene compound>

N-bromosuccinimide (552 mg) was dissolved in 20 mL of THF in a nitrogen atmosphere, and the resulting solution was cooled to -20°C, added to 0.33 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the resulting solution was
25 added to a solution of 150 mg of 6,13-dihydro-6,13-dihydroxy-2,3-dipropylpentacene dissolved in 15 mL of THF dropwise, and then the reaction was

carried out for 18 hours while being warmed up to room temperature.

triethylborohydride, and they were allowed to react with each other at room temperature for 2 hours in a nitrogen atmosphere. The resulting solution was neutralized with diluted aqueous hydrochloric acid, and the organic phase was separated, concentrated and dried under a vacuum to produce 2,3-diethyl-6,13-dihydro-6,13-dihydroxypentacene almost stoichiometrically.

<Method for producing polyacene compound>

N-chlorosuccinimide (300 mg) was dissolved in 40 mL of dichloromethane in a nitrogen atmosphere, and the resulting solution was cooled to -20°C , added to 0.3 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the resulting solution was added to a solution of 75 mg of 2,3-diethyl-6,13-dihydro-6,13-dihydroxypentacene dissolved in 4 mL of THF dropwise, and then the reaction was carried out for 18 hours while being warmed up to room temperature.

The reaction product was distilled under a vacuum to remove the organic solvent, and the resulting residue was washed with acetonitrile thoroughly. This produced 25 mg of pure 6,13-dichloro-2,3-diethylpentacene in a yield of 30%.

The resulting 6,13-dichloro-2,3-diethylpentacene was analyzed by mass spectrometry. The results are given below.

FAB-HRMS (NBA): $m/z=404, 402$

Moreover, it was analyzed by nuclear magnetic resonance spectroscopy (NMR) at room temperature with deuterated chloroform as a solvent. The results are given below.

^1H -NMR (ppm): δ 1.40 (t, 6H), 2.82 (q, 4H), 7.39 (dd, 2H),
7.78 (s, 2H), 8.00 (dd, 2H), 9.05 (s, 2H), 9.13 (s, 2H)

The transistor was analyzed for current/voltage curve between the source and drain electrodes with the silicon substrate as the gate, where the gate voltage was changed at 10 V intervals from -10 to -40 V. It was observed that the drain current was saturated as the drain voltage increased. Mobility determined from gate voltage dependence in the current saturated region was $5 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$.

<EXAMPLE 9: Synthesis of

6,13-dichloro-2,3-(methylenedioxy)pentacene>

10 <Synthesis of intermediate>

A solution of 57 mg of 2,3-methylenedioxy-6,13-pentacenequinone dissolved in 25 mL of THF was added to 1.6 mL of a 1 mol/1000 mL THF solution of lithium triethylborohydride, and they were allowed to react with each other at room temperature for 1 hour in a nitrogen atmosphere. The resulting solution was neutralized with diluted aqueous hydrochloric acid, and the organic phase was separated, concentrated and dried under a vacuum to produce 6,13-dihydro-6,13-dihydroxy-2,3-(methylenedioxy)pentacene almost stoichiometrically.

<Method for producing polyacene compound>

N-chlorosuccinimide (250 mg) was dissolved in 40 mL of dichloromethane in a nitrogen atmosphere, and the resulting solution was cooled to -20°C , added to 0.3 mL of dimethyl sulfide dropwise, and stirred for 10 minutes. Then, the solution was added to a solution of 57 mg of 6,13-dihydro-6,13-dihydroxy-2,3-(methylenedioxy)pentacene dissolved in 3